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13. ABSTRACT *(Maximum 200 words)*

This report concludes a nearly 4-year study of Shape Memory Alloys and development of new high temperature two-way shape memory alloys. New alloys were characterized in terms of their phase transformation temperatures, shape memory effect and mechanical properties. The work encompassed investigations of smart structures including NiTi-aluminum metal-metal composite materials. Development of high temperature SMAs extend use of applications to areas in which they are most needed, i.e., in defense and industrial fields that employ shape controlling and vibration depression in high temperature environments. Most of the research focused on the $(Ni_{50-x}X_x)$ Ti (X=Pd,Pt,Au) and NiMn-Ti systems, and investigation and training of NiTi-Pd, NiTi-Hf and NiTi-Zr two-way shape memory alloys.

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DEVELOPMENT OF HIGH TEMPERATURE TWO-WAY SHAPE MEMORY ALLOYS

FINAL TECHNICAL REPORT

Submitted by Dr. Kuang-Hsi Wu

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TABLE OF CONTENTS

1. FOREWORD

This report concludes a nearly four-year study of Shape Memory Alloys (SMAs), a very important smart material that acts as both a sensor and an actuator.
The unique ability of SMAs to remember and recover their original shape combined with their energetic recovery power and precise shape-temperature-stress response has stirred much excitement in this material's potential for defense and industrial applications. However, most currently used SMAs, including NiTi, Cu-Zn-Al and Cu-Ni-Al, have a phase transformation temperature below 100°C. This unfortunately hinders the application of the SMAs in high temperature environments, which are precisely where their application would be most useful. Many defense and industrial fields that employ shape controlling and vibration depression in high temperature environments would greatly benefit by using high temperature shape memory alloys. Obviously, it is an imperative to develop high temperature shape memory alloys.

Since the early 1970s scientists have worked steadily to harness the potential of shape memory alloys. At that time a few scientists began to study the effect of various metallurgical factors, such as composition and heat-treatment, on the martensite transformation temperature of the existing SMAs. They made attempts to elevate the transformation temperature of the shape memory alloys to more than 100°C, which proved to be a stubborn barrier. This was as far as the research went for the next twenty years and no further significant progress was made.

Recently, scientists have made inroads into research on newer, higher temperature shape memory alloys that have a phase transformation temperature much greater than that of the typically employed SMAs. Most of the research has focused on the $(Ni_{50-x}X_x)$ Ti (X=Pd, Pt, Au) and NiMn-Ti alloy systems because it is believed that these are the candidates with the highest potential for practical applications. Of the best candidate materials, which include the $(Ni_{50-x}Pd_x)$ Ti, $(Ni_{50-x}Pt_x)$ Ti, and $(Ni_{50-x}Au_x)$ Ti, systems, $(Ni_{50-x}Pd_x)$ Ti is believed to have the best potential. Disadvantages inherent in several systems are that $(Ni_{50-x}Pt_x)$ Ti is considered too expensive to be used in practice and $(Ni_{50-x}Au_x)$ Ti is not stable for thermal cycling. The transformation temperature of NiMn-Ti based alloys can reach to as high as 500°C, however, because these alloys are extremely brittle and unstable, it is recognized that this alloy is also not suitable for practical usage.

One-way shape memory in and of itself was a phenomenon worth celebrating, and the realization of two-way shape memory effect has led to even more advanced, innovative concepts for applications. Two-way memory alloys (TWSMAs) could memorize two configurations, as opposed to one. While the two-way memory effect became known in the mid-1970's, a complete understanding of the whole mechanism of the phenomenon has yet to be explained. TWSMAs have shown significant potential for use in defense purposes and private industry due to these compelling features. Typical potential applications include connectors for missile guidance systems, jet fighter hydraulic couplings, tank actuators, satellite components, computer and electronic components, as well as medical and robotics usage.

Recent literature reports that a few of the current low temperature SMAs, such as NiTi, CuAlNi, and CuZnAl, can demonstrate two-way memory effect after proper thermomechanical training. It is also reported that the two-way memory effect of those alloys strongly depends on the training procedures. However, there is little similar work that has been done on either one-way or two-way memory effects of high temperature shape memory alloys (HTSMAs).

2. RESEARCH OBJECTIVES

The objective of the project, "Development of High Temperature Two-Way Shape Memory Alloys," sponsored by the Army Research Office, was to explore a series of high temperature shape memory alloys that had the best potential to demonstrate one-way and two-way memory effect. Given the paucity of existing research on HTSMAs, the scope of this study was to focus on three aspects:

1) Develop more extensive studies of martensite transformation behavior and shape memory effect in NiTi-Pd alloys in order to establish enough engineering data for practical applications.

2) Search for innovative high temperature shape memory alloys in addition to the $(Ni_{50-x}Pd_x)Ti$ system and characterize their transformation temperature, mechanical properties, shape memory effect, two-way memory effect and stability.

3) Study the feasible two-way memory training procedures for high temperature shape memory alloys and optimize the two-way training process for potential candidate high temperature shape memory alloys.

Within the three focus areas, the main research goals were further defined to concentrate on:

- Martensite transformation behavior of $(Pd_xNi_{50-x})Ti_{50}$ and to deeply understand the role of various metallurgy factors on the martensite transformation temperature.

- Thermal cycling stability of NiTi-Pd alloys.

- Mechanical behavior of NiTi-Pd alloys.

- Rapid solidification process and melt spun approach to fabricate NiT-Pd ribbon.

- Search for innovative high temperature shape memory alloys and characterize their transformation temperature, mechanical properties, shape memory effect, two-way memory effect and stability.

- Martensite transformation behavior of new $(Hf_{xi}Ti_{50-x})Ni_{50}$, $(Zr_{xi}Ti_{50-x})Ni_{50}$, and $(Ni_xTi_{50-x})Mn$ alloy systems, and understand the role of various metallurgy factors on the martensite transformation temperature.

- Study crystal structures of various phases (parent, martensite, and second phases) involved in new $(Hf_{xi}Ti_{50-x})Ni_{50}$, $(Zr_{xi}Ti_{50-x})Ni_{50}$, and $(Ni_xTi_{50-x})Mn$ alloy systems.
- Shape memory effect and mechanical behavior of NiTi-Hf/ NiTi-Zr alloys.

- Study the feasible two-way memory training procedures for high temperature shape memory alloys and optimize the two-way training process for different potential candidate high temperature shape memory alloys.

- Two-way memory training of NiTi-Pd alloys.

- Two-way memory training of NiTi-Hf alloys.

- Two-way memory training of NiTi-Zr alloys.

3. SUMMARY OF THE MOST IMPORTANT RESULTS

3.1 NiTi Binary Alloys

Discovery that the R-phase in the binary alloys is a superior material for smart materials/structure applications in lieu of its short hysteresis (3-6°C as opposed to 20-40°C in the martensite), lower enthalpy involvement (faster heating and cooling rate), and minimum transformation volume change. Based on our thermodynamic calculation, the R-phase alloys can achieve a 6-10 times higher response rate than their martensite counterparts.

3.2 NiTi-Pd High Temperature Shape Memory Alloys

Although NiTi-Pd alloys are a promising candidate as a high temperature shape memory alloy there are also many problems that have to be addressed before this alloy achieves practical usage. In this project, the research addressed the following issues: shape memory effects, mechanical properties, thermomechanical stability, and two-way memory training procedures and two-way memory effect.

Detailed studies were conducted to investigate the thermomechanical stability of NiTi-Pd high temperature shape memory alloys. To compare with NiTi binary low temperature shape memory alloys, a series of NiTi binary alloys with different compositions were also used to study their thermomechanical stability. It was found that the transformation temperature change of NiTi-Pd alloys after 1000 times cycling decreases as the Pd addition increases. In comparison with the NiTi binary alloys, NiTi-Pd alloy has much better stability than NiTi binary alloys. For example, the transformation temperature change of NiTi-30at% Pd after 1000 times cycling is only 2°C compared to 30°C for Ni-50at%Ti alloy.

Out of this research a new theory was developed, described as a *dislocation thermodynamic model*, to describe enplanement stability of thermomechanical cycling of shape memory alloys. This new theory extends the existing theory to successfully enplane the thermal cycling effects of shape memory alloys. The dislocation thermodynamic model not only offers insight into the thermal cycling effect of shape memory alloys, one of the most important phenomena of shape memory alloy, but also provides various practical approaches to improve the stability of different high temperature shape memory alloys.

Since it is very difficult to prepare large samples of NiTi-Pd alloys, no one has heretofore reported on the mechanical properties and shape memory effects of this alloy, a necessary step that is essential to determine proper application. The investigators of this project are believed to be the first to report successful fabrication of large, standard tension samples and to systematically study the mechanical properties (stress-strain curve, Young's modulus, yield strength of martensite and austenites) and Shape Memory Effect (reversible strain, recovery stress) of NiTi-Pd high temperature shape memory alloy as a function of composition, temperature and strain rate. *The result of this work provides an extensive, essential and systematic database that makes new designs and applications of NiTi-Pd high temperature shape memory alloys possible.*

Few experimental results have been reported for two-way memory effect of shape memory alloys that possess a transformation temperature of more than 100°C, and none have been reported for the for the NiTi-Pd system. In this project, after establishing the database, the investigators proceeded to study ways to train the two-way memory of NiTi-Pd high temperature shape memory alloys and the various factors that affect these alloys. Particularly stringent learning methods were applied due to the fact that the investigators are also educators. It was discovered that the NiTi-Pd alloys could demonstrate improved two-way memory effects by employing an appropriate training procedure, even when the alloys had transformation temperatures over 500°C.

Because of the poor hot and cold workability of the NiTi-Pd alloys, it was very difficult to fabricate a section area of small diameter NiTi-Pd wire using typical methods. Logic dictated the decision to investigate the use of a melt-spun method to fabricate NiTi-Pd ribbons, and this was successfully accomplished. Factors studied included the influence of process parameters (such as cooling rate, heat treatments, compositions) on the quality (thickness, wideness, surface roughness, contamination), microstructure (grain size, orientation, and distribution along the cross section), shape memory effect, and mechanical properties of the NiTi-Pd ribbons. Results of this study showed that uniform NiTi-Pd ribbons can be fabricated using a melt-spun method. Shape memory effect and mechanical properties were most influenced by the cooling rate and the heat treatment. More uniform spun ribbons were possible in alloys with a higher Pd content. The preferred grain orientation in the ribbon cross section proved to be a disadvantage in maintaining shape memory effect.

3.3 NiTi-Hf High Temperature Shape Memory Alloys

Although NiTi-Pd alloys possess qualities that allow high transformation temperature and good shape memory effect, they are very expensive due to the alloying element, Pd. Thus it was necessary to continue the search for more economical materials which possess similar mechanical properties and shape memory effect as NiTi-Pd. In the NiTi-Pd alloys, Pd substitutes for the Ni element in Ni-Ti binary alloys. A search through the literature revealed that no studies have been done to determine what would happen if an alloying element was substituted for Ti in Ni-Ti binary compounds, and so the investigators undertook this task. Preliminary studies found that the transformation temperature of NiTi alloys increase when Ti is substituted by Hf or Zr. Because the price of the raw Hf element is only 1/6 that of Pd, there is reasonable expectation that NiTi-Hf alloys will prove more economical to use than NiTi-Pd alloys. Thus, the development of NiTi-Hf high temperature shape memory alloys have warranted special attention.

3.3.1 A New NiTiHf Alloy

After three years of hard work, we have successfully developed a new economical Ni50-(50-x)Ti-xHf high temperature shape memory alloy. The newly developed NiTi-Hf alloy has a much higher transformation temperature than the NiTi-Pd and NiTi-Pt alloys with the same atomic percentage of the third alloying elements. The NiTiHf high temperature shape memory alloys cost 1/6 to 1/10 of the cost of NiTi-Pd to produce due to the lower price of Hf element and the smaller amount of Hf required to achieve the same transformation temperatures. Meanwhile, the shape memory effect of the new alloys is compatible with the NiTi-Pd alloys. Considering the shape memory effect and the costs, the NiTi-Hf alloys have been recognized as the alloys with great potential for high temperature applications.

The main studies and important results are as follows:

A detailed investigation was carried out to study martensite transformation behavior of NiTi-Hf high temperature shape memory alloys. The experimental results were:

1) An addition of more than 5% hafnium can significantly elevate the phase transformation temperature. When the concentration of hafnium is 30at%, the austenite transformation temperature can reach 450°C, but the initial addition of hafnium depresses the transformation temperature.

2) The chemical driving force decreases with the Hf content in the monoclinic B19′ region and increases in the orthorhombic B19 region. The ΔS decreases in the monoclinic martensite region and remains almost constant in the orthorhombic martensite.

3) The addition of Hf does not change the hysteresis behavior of NiTi alloys. The martensite transformation in the NiTi-Hf alloys is thermoelastic.

4) The NiTi-Hf alloys have better stability in the thermal cycling process than NiTi binary alloy. The change in transformation temperature during the thermal cycling process decreases as the Hf content increases. For the NiTi-25at% alloys, the change in transformation temperature after 100 times cycling is only 7°C compared with 30°C for NiTi binary alloy.

More data was necessary to augment these results since a search of the literature turned up nothing. A systematic experiment was then conducted to study the crystal structure, the microstructure, and the distribution of the involved phases of NiTi-Hf alloys as a function of composition and temperature. The main results were:

1) The crystal structure of the high temperature parent phase is a CsCl-type when the Hf content is in a range of zero to 30at%. The lattice parameters of the parent in these NiTi-Hf alloys decreases with an initial addition of Hf and then significantly increases as more Hf is added.

2) Addition of Hf makes the transition of martensite structure from monoclinic to orthorhombic. The main product of the martensite transformation for alloys with X <6 is monoclinic B19′ martensite. In addition, the R-phase is also present. However, for the alloy with $X \geq 12.5$, the main product is orthorhombic B19.

3) The second phase, formed upon solidification, has the same crystal structure when the Hf content is in a range of zero to 30at%. The second phase, $(Ti_{1-x}Hf_x)_2Ni$, has the same crystal structure as Ti_2Ni in the Ti-Ni binary system.

4) The stability of the martensite structure of TiNi-X systems can be successfully predicted using Pettifer's phenomenological method. The martensite structure changes from monoclinic to orthorhomobic when the $M_{Ni} > 1.58M_{Ti} - 13.6$.

The shape memory effects of NiTi-Hf alloys were carefully characterized. The main results are as follows:

1) The alloys based on NiTi-Hf demonstrate complete shape memory effect even when the Hf content was 30at%.

2) The fully reversible strain, ε_c, decreases gradually as the Hf content increases, which is associated with increasing resistance to the twinning, and the increased volume of the Hf content in the second phase.

3) The shape memory alloy deteriorates as the deformation temperature increases. The degrees in the deterioration of the shape memory effect are different in different deformation temperature ranges. When the temperature is below 120°C, the shape memory effect deteriorates slightly as the temperature increases, and there is only a small difference between the curve of the recovery percent versus pre-strain at room

temperature and 120°C.

Various two-way memory training procedures were applied to NiTi-Hf alloys. The main results are as follows:

1) The NiTi-Hf alloys demonstrated an obvious two-way memory effect after proper thermomechanical training. The two-way memory effect increased as the pre-strain increased, which is associated with the increasing of residual strain with increasing pre-strain.

2) The high transformation temperature is harmful to the two-way memory effect, which is confirmed by the fact that the two-way memory effect deteriorates as the heating temperature increases.

Based on the results of the transformation behaviors, phase crystal structure and shape memory effect, it was recognized that the NiTi-Hf alloys possess qualities that were as capable of achieving good shape memory effect as the NiTi-Pd alloys. The NiTi-Hf alloy is an excellent candidate to substitute for expensive NiTi-Pd alloys.

Although the above mentioned merits of newly-developed NiTi-Hf alloys are extensive, there are still many problems that need to be solved before applications become widespread. In our initial investigation, the main focus was placed on how to increase the transformation temperature of NiTi alloys using more economical alloying elements. Due to the time frame, little attention was allocated to improving the shape memory effect. Although demonstrating a compatible shape memory effect with NiTi-Pd alloys, the NiTi-Hf alloys are still considered to have inferior shape memory properties. However, this does not mean that NiTiHf would be limited by these problems. The fact is that, so far, no efforts have been made to improve the alloys through any known techniques. The main shortcomings of the NiTi-Hf high temperature shape memory alloys, in comparison with the NiTi-based low temperature shape memory alloys, are summarized as follows:

- Low Fully Reversible Strain
- Low Ductility
- Lower Two-Way Memory Effect

Low fully reversible strain. Figure 1 summarizes the fully reversible strain of the NiTi-Hf high temperature shape memory alloys as a function of the Hf content. It shows that the fully reversible strain of the NiTi-Hf alloys dramatically decreases as the Hf content increases. When the Hf content reaches 30at% (the transformation temperature reaches about 400°C), the fully reversible strain decreases to 1%.

Low ductility. The newly-developed NiTi-Hf alloys, especially high Hf containing alloys, are very brittle. This not only limits the application of the alloys, but also hinders the cold and hot deformation, as well as lowers the possibility of two-way memory training of the alloys. Figure 2 shows the tensile elongation of NiTi-Hf alloys as a function of the Hf content. It clearly shows that the ductility of the alloys dramatically decreases as the Hf content increases.

Lower two-way memory effect. It was proven in our previous study that the NiTi-Hf high temperature shape memory alloys can demonstrate two-way memory effect through proper training, and the two-way memory effect increases as the training strain increases. However, because of its poor ductility, the training strain that can be achieved is generally quite low. Due to this strain limitation, the NiTi-Hf alloys can only be trained to have a small amount of two-way memory strain.

The objective of this phase of the research was to improve the shape memory effect and mechanical properties of the NiTi-Hf high temperature shape memory alloys through microalloying, and accurately controlling stoichiometry and microstructures. It was anticipated that through these processes, *the performance of NiTi-Hf alloys could be significantly improved to match NiTi alloys, and meet the challenge of the requirement for smart materials/structures applications.*

Based on our investigation, it was found that there were two main factors that were responsible for the lower shape memory effects and the poor ductility of the NiTi-Hf alloys. One comes from the intrinsic deformation characteristics of NiTi-Hf alloys; the other results from the existing large amount of second phases.

Basically, there are two methods to provide a macro-deformation of martensite in shape memory alloys. One corresponds to the movements of the twin boundaries (so-called detwinning) and the other associates with dislocation slipping. Only a certain amount of martensite deformation can be accommodated by the detwinning process, and the deformation accompanied by detwinning can be fully recovered after heating the sample into austenite. When the deformation amount exceeds this level, the dislocation will begin to slip, and the deformation associated with the dislocation slipping is irreversible by heating the sample into austenite. Therefore, the fully reversible strain of the shape memory alloys is equivalent to the maximum deformation that the detwinning process of martensite can provide before the dislocation slipping, which corresponds to the plateau in the stress-strain curve.

In the NiTi-Hf alloys, the amount of second phase $(Ti_yHf_{100-y})_2Ni)$, increases as the Hf content increases, as shown in Fig. 3. The increase of the second phase results in a deterioration of both shape memory effect and ductility. Because the second phase does not undergo martensite transformation, it follows that the greater the amount of second phase, the lower the full recovery strain. In addition, the existence of the second phase causes the materials to become brittle. Figure 4 shows the fracture surface of the tension samples of the NiTi-Hf alloys as a function of the Hf content. Note that the area of the brittle cleavage facet increases as the Hf content increases. The cleavage facet is not easy to observe below 5 at% Hf and becomes more obvious when the Hf content is more than 20 at%. Analysis of the composition of the brittle cleavage facet area and the surrounding ductile region shows that the cleavage facet corresponds to the $(Ti_yHf_{100-y})_2Ni$ second phase and the surrounding ductile area is a martensite matrix. Therefore, it can be deduced that the increase of the second phase is the main reason for the brittleness of the high Hf-containing alloys.

After understanding the two factors that are responsible for the inferior shape memory effect and ductility of the new NiTi-Hf alloys, we have proposed two approaches to solve these two problems respectively. They are as follows:

3.3.2. Addition of a Cu Replacement for Hf

Copper is a main element in the low temperature NiTi based shape memory alloys. The NiTi-(10-15 at%)Cu alloy is a well-known low temperature shape memory alloy, and has as good a shape memory effect as the NiTi binary alloys. A primary feature of NiTi-Cu alloys is that the martensite is orthorhombic when the Cu content is more than 10 at%. Thus, it is possible to use 10 at% Cu for replacing 10 at% Hf to change the martensite structure. Then based on the NiTi-10 at% Cu alloys, the Hf element will be added to increase the transformation temperature. Since the addition of Cu does not deteriorate the shape memory effect of NiTi alloys, the addition of Cu, substitution of Hf, is considered to be effective in order to lessen the deterioration of Hf to the shape memory effect. In addition, because of the much lower cost of Cu than Hf, the costs of the final alloys will be greatly reduced.

In the NiTi-Hf alloys, the transformation temperature increases with the increase of the Hf content only if the martensite structure is orthorhombic. In the monoclinic regions, the transformation temperature decreases as the Hf content increases, as shown in Fig. 5. The transmission of martensite structure from monoclinic to orthorhombic takes place only when the Hf content is more than 10 at%. Therefore, the effective Hf content in the NiTi-xHf alloys, used to increase the transformation temperature, is only x-10. For example, in NiTi-20 at% Hf alloys, only 10at% Hf were used to increase the transformation temperature, and the remainder is used to transmit the martensite structure. If we use other alloying elements, which can transmit the martensite structure from monoclinic to orthorhombic, to replace the 10 at% Hf, then we can abate the deterioration of the Hf to the shape memory effect.

3.3.3. Controlling the Stoichiometry to Avoid Second Phase

The formation of the second phase, $(Ti_yHf_{100-y})_2Ni$, is mainly caused from the fact that the alloy undergoes the $B2+(Ti_{1-x}Hf_x)_2Ni$ two phases field during the initial solidification process. In order to avoid the formation of the second phase, the stoichiometry of the alloys needs to be accurately controlled. This is difficult for ternary alloys if we do not have the Ni-Ti-Hf ternary phase diagrams. In our group, we have conducted a primary investigation on the phases equilibrium behavior at high temperature and have acquired an approximate composition region in which the NiTi-Hf exists in a single B2 field.

Based on these proposed approaches, we have prepared a variety of NiTi-Hf-Cu samples to test the proposed approaches. The primary tests show very positive results. However, because the project has officially ended, we lack additional funding to continue to investigate the potential and application of this information.

3.4. NiTi-Zr High Temperature Shape Memory Alloys

Another high temperature, economically friendly candidate, NiTi-Zr alloy, was investigated to characterize phase transformation behavior and shape memory effect.

The main studies and important results are as follows:

The addition of more than 5at% Zr can significantly elevate the phase transformation temperature. The chemical driving force decreases with the Zr content in the monoclinic B19′ region and increases in the orthorhombic B19 region. The ΔS decreases in the monoclinic martensite region and remains almost constant in the orthorhombic martensite. The NiTi-Zr alloys have poorer stability in the thermal cycling process than the NiTi-Hf alloys.

The first experimental investigation studied the crystal structure, microstructure, and distribution of all of the involved phases of NiTi-Zr alloys as a function of composition, and temperature. It was found that the crystal structure of the high temperature parent phase is a CsCl-type when the Zr content is in a range of zero to 20at%.

Addition of Zr also enabled a transition of martensite structure from monoclinic to orthorhombic. The main product of the martensite transformation for alloys with Zr content smaller than <6 was monoclinic B19′ martensite, but for the alloys with Zr content more than 10at% the main product was orthorhombic B19. Two types of second phases formed in the NITi-Zr alloys. One was $(Ti_{1-x}Zr_x)_2Ni$; the other has not yet been identified.

The shape memory effect of NiTi-Zr alloys were preliminarily characterized. The main results were as follows:

The alloys based on NiTi-Zr demonstrate complete shape memory effect even with a Zr content of 20at%; the fully reversible strain decreases gradually as the Zr content increases. However, the fully reversible strain of NiTi-Zr alloys is much smaller than NiTi-Hf alloys at the same transformation temperature. The NiTi-Zr alloys also demonstrated two-way memory effect after proper thermomechanical training.

In conclusion, *NiTi-Zr alloys can join other high temperature shape memory alloys as an economical candidate for military or industrial applications.* The brittleness, poor workability and stability, and relatively low shape memory effect are the main hindrances for the immediate application of this alloy. The investigators are confident that studies continuing this preliminary work would lead to solutions to improve ductility and hot workability of the NiTi-Zr alloys.

3.5 New High Temperature Two-Way Shape Memory Alloys

The FIU team developed new high temperature two-way shape memory alloys. Alloys of TiV, TiVCr, TiVFe, TiZrHfNi with various compositions were fabricated. The objective of this phase was to characterize the new alloys in terms of their phase transformation temperatures, shape memory effect (one-way and two-way), and mechanical properties. Hopefully, new high temperature SMAs will be developed through this effort.

3.5.1 NiMn-Ti High Temperature Shape Memory Alloys

NiMn is a possible candidate as a useful high temperature shape memory alloy. Characterized by a very wide hysteresis width (70°C), the martensite transformation is not fully reversible. The investigators discovered that the Ti alloying element can successfully reduce the thermal hysteresis width and adjust transformation temperature. This makes it possible for NiMn-Ti alloys to fully recover its pre-deformation shape. A preliminary study shows that NiMn alloy possess shape memory effect that surpasses the other alloys thus reported. Again, the main problem of this material is its extreme brittleness. Further research is needed.

3.5.2 Smart Structures

The FIU team pioneered work on NiTi-Aluminum metal-metal composite materials. The differential gradient interface layers of TaO and NiTi were successfully built on a NiTi wire, which was embedded in the aluminum matrix. Both resistance measurement and vibration measurements indicated that the layer can provide insulation of the NiTi wire and can be used for vibration suppression for smart structures. A paper was presented at the Fourth International Conference on Adaptive Structures, November 1993, in Germany.

There remains important work to be completed in order to establish a new and fundamental data base and to improve the performance level compatibility with existing high temperature SMAs.

4. LISTS OF PUBLICATIONS, CONFERENCES AND TECHNICAL REPORTS

Significant developments have been accomplished and substantial technical information has been presented or published in journals or at conferences. Among several materials studied in the past three years, NiTiHf alloys have been identified as the material with the greatest potential for high temperature two-way shape memory alloy (TWSMA) applications, a finding that has created great interest in the scientific community.

Publications & Conferences:

1. Y. Gao, K. H. Wu, Y. Q. Li, "In-Situ Observation of Deformation Associated with R-Phase in NiTi SMA, to be presented at the 1995 MRS Fall Meeting, Boston, MA, Nov. 27 - Dec. 1, 1995.

2. K. H. Pu and Z. J. Pu, "Thermodynamic Analysis of Martensite Transformation in High Temperature SMAs," to be presented at the 1995 MRS Fall Meeting, Boston, MA, Nov. 27 - Dec. 1, 1995.

3. Z. J. Pu, S. Dalip, Y.Q. Liu, H.K. H. Wu, "Development of a Constitutive Shape Memory Alloy Damping Model, to be presented at the 6th International Conference on Adaptive Structures, Key West, FL, Nov. 13-15, 1995.

4. K. H. Wu, F. Yang, J. Shi and Z. J. Pu, "Rate Sensitive Behavior and Modeling of Shape Memory Alloys, to be presented at the 6th International Conference on Adaptive Structures, Key West, FL, Nov. 13-15, 1995.

5. K. H. Wu, "Martensitic Transformation of $(Hf_xTi_{50-x})Ni$ Shape Memory Alloys," presented at International Conference on Martensitic Transformations, August 20-25, 1995, Lausanne, Switzerland; to be published in *Journal de Physique.*

6. M. Carballo, Z. Pu, and K. H. Wu,"Variation of Electrical Resistance and the Elastic Modulus of Shape Memory Alloys under Different Loading and Temperature Conditions," *Journal of Intelligent Materials and Structures*, July, 1995.

7. Z. J. Pu, H. K. Tseng and K. H. Wu, "Shape Memory Effect and Mechanical Properties of NiTi-Zr High Temperature Shape Memory Alloys", *Proceedings*, 1995 North American Conference on Smart Materials and Structures, Feb. 1995, San Diego, CA, p. 171.

8. J. Li , D. Yang & K. Wu, "Influence of Heat Treatment on The Transformation Hysteresis of Cu-Al-Ni-Mn-Ti Shape Memory Alloys," *Journal of Material Science* V (1993) P.

9. Z. Pu & K. Wu, "Martensitic Transformation of Ti50-Ni(50-x)-X Pd High Temperature Shape Memory Alloys," *Journal of Applied Physics*, in Press.

10. K. H. Wu,"Study of Cooling Characteristics of Shape Memory Alloys and composites," (invited paper), Proceeding of Symposium on Active Materials and Smart Structures, October 1994, Houston, Texas.

11. K. H. Wu,"Study of Cooling Characteristics of Shape Memory Alloys and Composites" *Journal of Intelligent Materials and Structures.*

12. Z. J. Pu, K. H. Wu H. K. Tseng and C. M. Wayman "A New High Temperature Shape Memory Alloy Based on NiTi-Hf System, Part 1 Transformation Behavior", Submitted to *Journal of Materials Science.*

13. Z. J. Pu, K. H. Wu, H. K. Tseng and C. M. Wayman, "A New High Temperature Shape Memory Alloy Based on NiTi-Hf System, Part 2, Microstructure and Structure" Submitted to *Journal of Material Science.*

14. Z. J. Pu, K. H. Wu, H. K. Tseng and C. M. Wayman "A New High Temperature Shape Memory Alloy Based on NiTi-Hf system, Part 3, Shape Memory Effect," Submitted to *Journal of Materials Science.*

15. K. H. Wu, Y. Q. Liu, M. Carballo, "Inter-Phase Stresses and Cycle Responses on SMA Composites," Proceedings, 1994 MRS Fall Meeting, Boston, MA, Nov. 1994.

16. Y.Q.Liu, Z.J.Pu and K.H.Wu,"Study of Cooling Characteristics and Shape Memory Effect of R-phase Alloys" International Symposium and Exhibition on Shape Memory Materials, Sept. 25-28, 1994, Beijing, China, 154.

17. Z. J. Pu, K. H. Wu and Y. Q. Liu, "Structure and Properties of Rapid Solidified High Temperature Shape Memory Alloys," *Proceedings,* International Symposium and Exhibition on Shape Memory Materials, Sept. 25-28, 1994, Beijing, China, p292.

18. Y. R. Zhu, Z. J. Pu and K. H. Wu, "The Stability of NiTi-Pd and NiTi-Hf High Temperature Shape Memory Alloys," *Proceeding*, International Symposium and Exhibition on Shape Memory Materials, Sept. 25-28, 1994, Beijing, China, p253.

19. C. Li and K. H. Wu," The Thermodynamic Approach of Studying the Thermal Cycling Effect on NiTi Shape Memory Alloys," *Proceedings,* International Symposium and Exhibition on Shape Memory Materials, Sept. 25-28, 1994, Beijing, China, p74.

20. Z. J. Pu and K. H. Wu, "The Martensite Transformation of NiTi-Hf High Temperature Shape Memory Alloys," *Proceedings*, Solid-Solid Phase Transformations in Inorganic Materials 94 Conference, July,1994, p 767.

21. K. H. Wu and L. Sun, "Training of NiTi-Pd High Temperature Shape Memory Alloys for Two-Way Memory Effect," *Proceedings,* First International Conference on Shape Memory and Superelastic Technologies, March 6-10, 1994, Monterey, California, p. 67.

22. L. Sun and K. H. Wu,"The Two-Way Memory Effect (TWME) In NiTi-Pd High Temperature Shape Memory Alloys," Proceedings of the International Society for Optical Engineering, 2189 -Smart Structure and Materials, February 14-16, 1994,

Orlando, Florida, ed. by Vijay K. Varadan, p. 298-305.

23. K. H. Wu and H. K. Tseng, and Z. J. Pu,"Shape Memory Effects of NiTi-Hf High Temperature Shape Memory Alloy" *Proceedings*, First International Conference on Shape Memory and Superelastic Technologies, March 6-10, 1994, Monterey, California, p. 61.

24. Z. Pu, H. K. Tseng, and K. H. Wu, "An Innovative System of High Temperature Shape Memory Alloys," *Proceedings*, International Society for Optical Engineering, 2189 - Smart Structure and Materials, February 14-16, 1994, Orlando, Florida, ed. by Vijay K. Varadan, p. 289-297.

25. C. Li and K. H. Wu, "Systematic Study of the Damping Characteristics of Shape Memory Alloys," *Proceedings*, International Society for Optical Engineering, 2189 - Smart Structure and Materials, February 14-16, 1994, Orlando, Florida, ed. by Vijay K. Varadan, p. 314-325.

26. K. Wu and D. Z. Yang, "Shape Memory Alloys and Their Applications," *Proceedings*, Chinese American Scholar Association of Florida, 1993 Annual Meeting, June 18-20, 1993, Tampa, FL, pp.

27. K. H. Wu and Z. J. Pu, "High Temperature Shape Memory Alloys," *Proceedings*, Second International Conference on Intelligent Materials, June 5-8, 1994, Williamsburg, VA.(Invited presentation.)

28. D. Z. Yang, Z. Pu and K. H. Wu, "A Metal Based Intelligent Composite with SMA Materials," Proceeding of the Fourth International Conference on Adaptive Structures, November, 2-4, 1993, Cologne, Germany, p. 405-417.

29. K. H. Wu, Y. R. Zhu, and L. Chen, "The Martensitic Transformation and Stability of the TiNi-Pd Shape Memory Alloy," *Proceedings*, 1992 Materials Research Society (MRS) Fall Meeting, Nov. 30-Dec. 4, 1992.

30. K. H. Wu, "Structure and Properties of Rapidly Solidified Nitinol Materials," Proceedings of the Materials Research Society Fall Meeting, Boston, Massachusetts, December 3-5, 1991, p. 361

Technical Reports:

1. Li Chen: "Thermal Stability and Corrosion Behavior of NiTi and NiTiPd Shape Memory Alloys," Master Thesis, 1994.

2. Hsien-Kuei Tseng: "NiTi-(Hf,Zr,Pd) High Temperature Shape Memory Alloys," Master Thesis, 1995.

3. Maritza Carballo: (Work in Progress) Ms. Carballo is the third student who will receive her Master's degree, based upon her work on the SMA AASERT project. Her work is still in progress and has not yet been named.

5. EQUIPMENT ACQUISITION

A differential scanning calorimeter, Thermal Analyst 2100, a power supply, speed was, extensometer, furnace, microscope lens, cool access autofil, two pc computers and one HP printer were purchased for this project. The College of Engineering at FIU has agreed to maintain service and repair costs.

6. PERSONNEL

Kuang-Hsi Wu, Principle Investigator

Dr. Wu was the principle investigator on the SMA project. He performed research and supervised a team that he put together to work on the project. Individual team members changed as certain stages were completed. The results of the work have been presented at conferences in California, Massachusetts, Germany, Florida, and China. The list of co-authors reflects the diversity and talent lent to the project throughout its various manifestations.

Dr. Wu moved from associate to full professor at Florida International University during the course of this project. He received his Ph.D. in Mechanical Engineering from University of Illinois at Urbana-Champaign in 1984. Dr. Wu has been working in the field of materials and mechanics for the past ten years. During that time, he has secured more than $2.3 million as a P.I. and 0.8 million as Co-P.I. in funding in the form of research and equipment grants from federal, state, and industrial agencies. Dr. Wu has been awarded outstanding Achievement Award in 1990, Outstanding Teaching Award in 1991 and Outstanding Research Award in 1993 by FIU to recognize his contribution and performance. In addition, he has also been involved two summer research with the Oak Ridge National Laboratory (ORNL) on subjects such as (1) Reaction Sintering of Nickel Aluminide Ni_3Al, (2) High Strain Rate Testing of Iridium Doped and Undoped Materials, and (3) Indentation Fracture of Si_3N_4 Ceramics.

Dr. Zhongjie Pu, Ph.D. Visiting Assistant Professor, F.I.U.

Dr. Pu received his Ph.D. from the Department of Metal Physical Metallurgy, Central Iron & Steel Research Institute (CISRI) in Beijing, China in 1990. During the period 1986-90, he worked as Co-P.I. on a project from the China Nature Science Foundation (CNSF), and completed his Ph.D. dissertation entitled "The Fracture and Deformation Behavior and Ductile Approach to Gamma TiAl-Based Alloys." Soon after his graduation, he worked as an Assistant Professor (June 1990 - June 1992) and Associate Professor (June 1992 - September 1992) at CISRI. He has been very active in research in the area of intermetallic compounds. Dr. Pu has secured four research projects from CNSF as either principal investigator or Co-P.I. He also secured two research projects from China High Technology Program as a Co-P.I. He has published more than 50 papers in refereed journals and refereed conference proceedings. He has been granted one patent in China. Most recently, he has succeeded in developing a Ti-rich TiAl-based alloy and high temperature shape memory alloys.

He has been a visiting professor at FIU since 1992.

Dr. C. M. Wayman

Dr. Wayman served as a consultant on this project and co-authored three articles. Dr. Wayman is a professor of metallurgy at the University of Illinois, Champaign, Illinois. He received his Ph.D. in metallurgy from Lehigh University in 1957. He is an acknowledged expert in the field of martensitic transformation and has written a book on the crystallography of martensitic transformations, contributed chapters to 10 others, and has authored or co-authored some 170 papers on martensitic transformations, thin films and electron microscopy. In 1969 has was a Visiting Professor at the University of Cambridge, and also NATO lecturer, Guggenheim Fellow and an Overseas Fellow of Churchill College. In 1978 he received the TMS-AIME Mathewson Gold Medal for "Outstanding contributions to the study of thermoelastic martensite transformations in alloys." In 1990 he was awarded an Honorary Professorship at Dalian University of Technology (Dalian, China).

Dr. Da-Zhi Yang

Dr. Yang was a visiting professor and part of FIU's Dalian University Research Exchange Program. Dr. Yang is a professor at the Department of Materials Engineering at Dalian University and was also a visiting scholar at the University of Illinois with Professor Wayman for two years. Dr. Yang is currently professor and Director of the Dalian Research Institute of Memory Alloys. His expertise is in the area of Cu-based and dual-phase SMAs. Dr. Yang co-authored several papers with Dr. Wu relating to this project.

Dr. Yu-Ru Zhu

Dr. Zhu was a visiting professor from Dept. of Materials Science at Shanghai Jiao-Tong University (China). She worked on the SMA project for one year at Florida International University. Dr. Zhu's work included x-ray diffraction, TEM/SEM and microprobe studies. Dr. Zhu co-authored several papers relating to this project with Dr. Wu.

Hsien-Kuei (Solomon) Tseng

(Completed Master's Thesis, 1995 - Copy attached)

Solomon Tseng worked very closely with the principle investigator and co-authored several papers that were subsequently published and/or presented at professional conferences.

His area of research focused on a thorough study of the Ni-Ti-(Hf,Zr,Pd) High Temperature Shape Memory Alloys, and he satisfied his master's thesis requirement through his work on these new alloys. He has made substantial contributions to knowledge of the NiTi-based SMAs. He was able to attend the First North American Conference on Smart Materials and Structures, held in Orlando, FL in February, 1994.

Chen Li

(Completed Master's Thesis, 1994 - Copy attached) Chen Li worked for more than a year on the project and her work necessitated a trip to University of Florida to use the MAIC Lab.

Kun Ji

Kun Ji was a graduate student who earned his master's degree during the time he worked on this project, however, the thesis was not written on the topic of HTSMAs. He worked closely with Li Chen.

L. Sun

L. Sun was a graduate student who spent two semesters on this project before transferring to the University of Virginia to complete his master's degree in mechanical engineering.
L. Sun co-authored several research papers with Dr. Wu.

Sacha Dalip:

Sacha Dalip is a undergraduate student who involved in this project for one and half years. He conducted the testing of internal friction of during martensite transformation. He also conducted mechanical testing, and sample material preparation and numerical analysis of shape memory composites. He was also involved in the design and construction of fatigue machine. This machine enabled our group to test fatigue properties of various shape memory wires. During this time, he has co-authored two papers which are presented on North American Conference on Smart Materials and Structures, 1995, San Diego, CA. and sixth international conference on adaptive structure, Key West, U.S.A. Nov. 1995. After two year training in materials science, he has been provided a scholarship from Iowa University to enter Ph. D program.

Special Acknowledgement

The FIU team would like to thank Dr. Wilbur Simmons for his patience, advice and unfailing encouragement warmly given to the students and visiting professors and who worked so diligently on this project, as well as to the principle investigators.

7. ILLUSTRATIONS

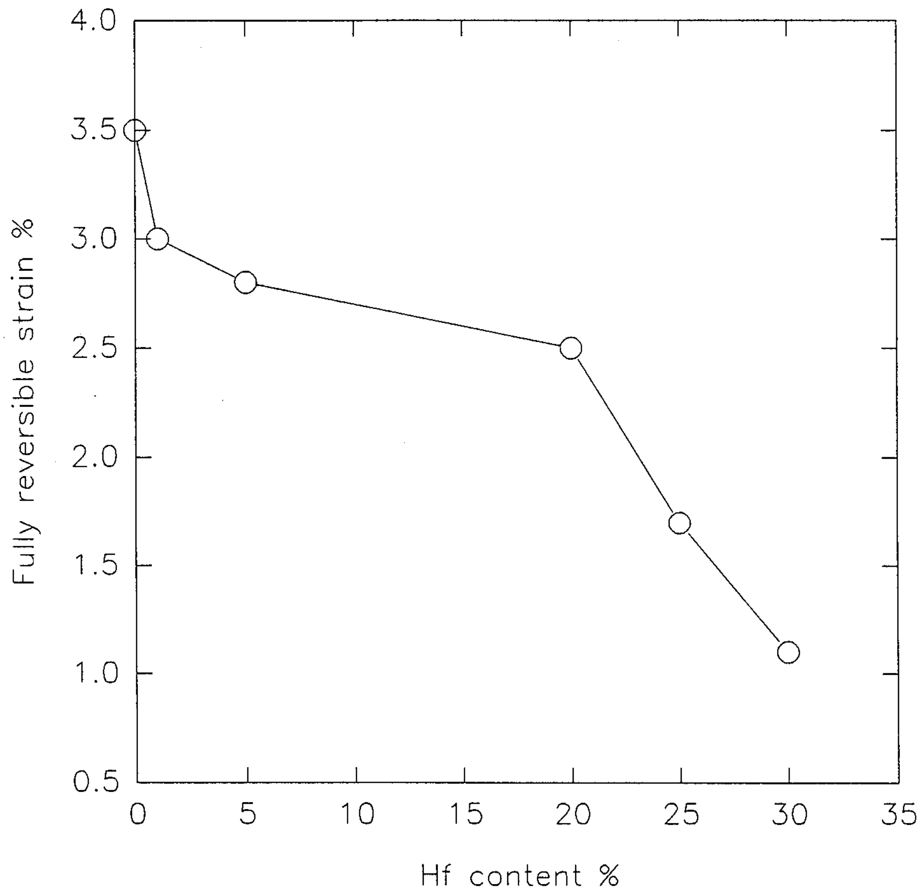

Figure 1.The fully reversible strain of NiTi–Hf high temperature shape memory alloys

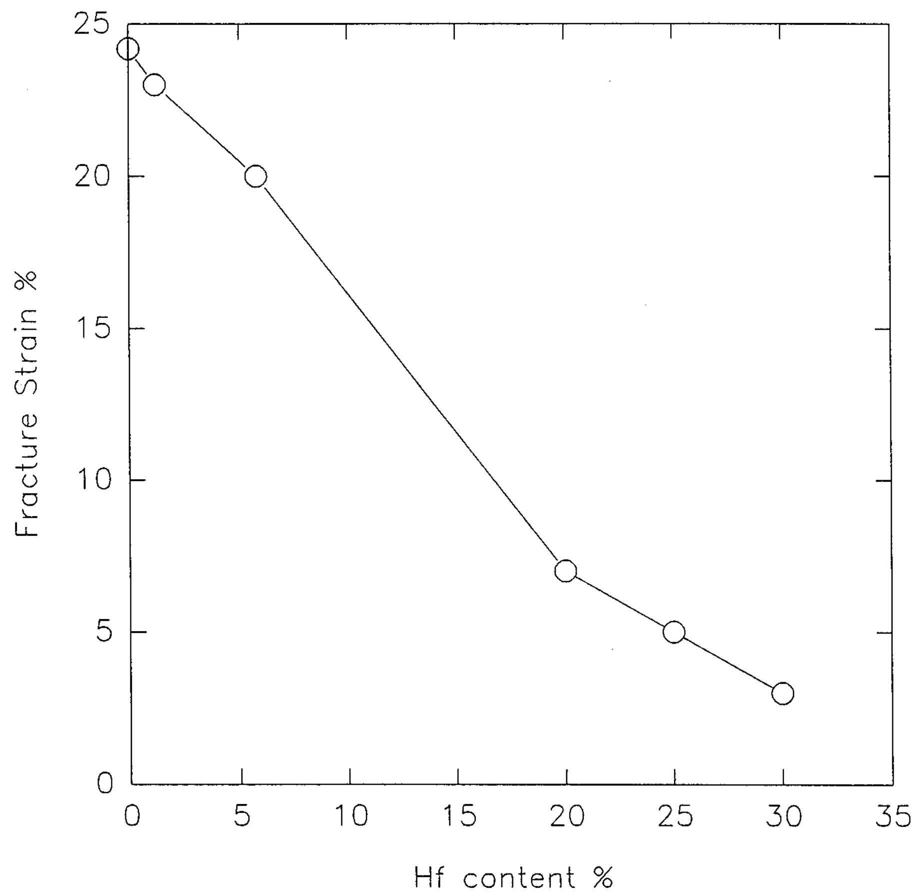

Figure 2. The fracture strain of NiTi–Hf alloys as a function of the Hf content

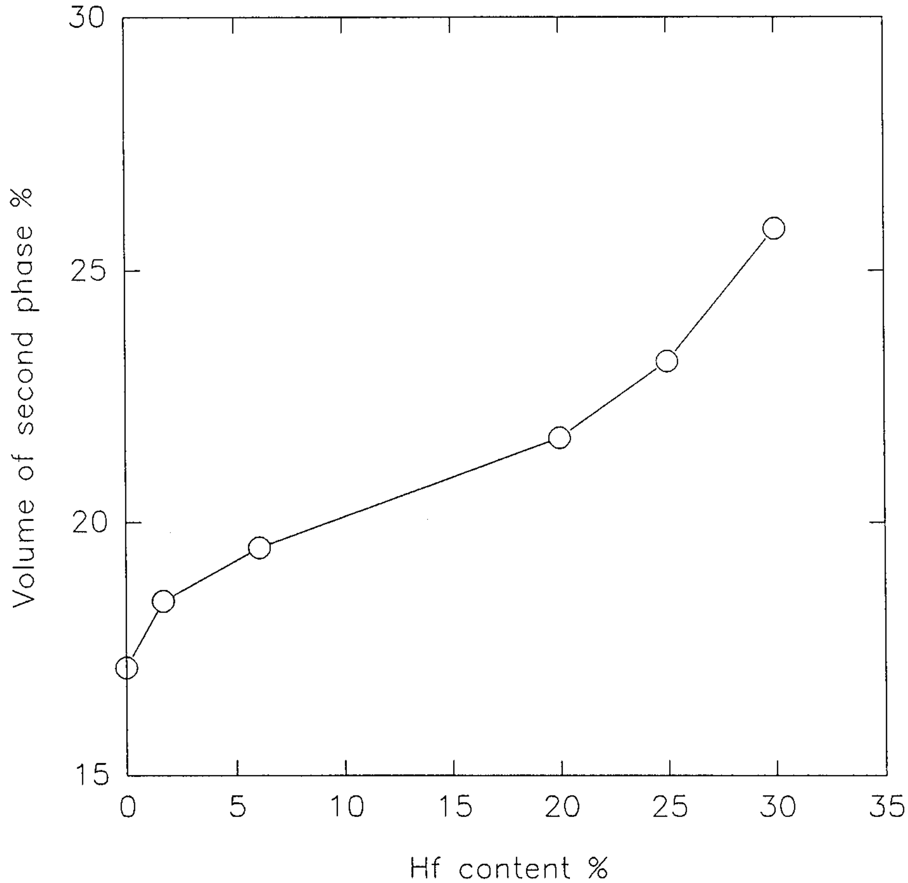

Figure 3. The amount of second phase of NiTi–Hf alloys as a function of the Hf content

Figure 4. The Fracture surface of NiTi-Hf alloys at room temperature, a, b, c, d, e, f are respectively to 0, 1, 6, 20, 25, 30 at% Hf alloys .

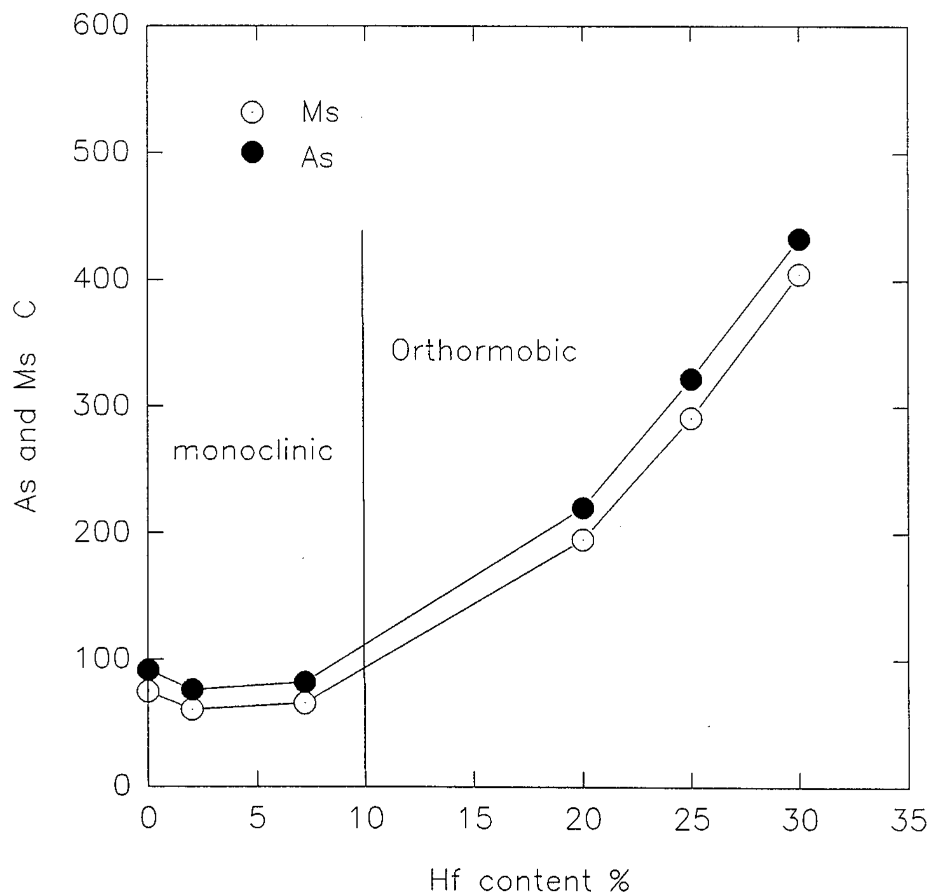

Figure 5. The transformation temperature of NiTi–Hf alloys as a function of Hf content